

Electronic Supplementary Information (ESI):

Direct preparation of semiconductor iron sulfide nanocrystals from natural pyrite

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Experimental Methods

1 Materials

Natural pyrites obtained from South Sichuan, China were ground to < 1000 mesh. Purified water was provided by the Water Purification System (HMC-WS10, Korea). ODX was synthesized as reported^[5]. Octadecyl amine (ODA) was purchased from the Changzhou Xinhua Active Material Research Institute, Jiangsu, China. Other reagents used in the study were of analytical grade.

2 Method

For the organic phase selection (OPS) process, ground pyrite and ODA were melted together at 120 °C and stirred for 1 h to enhance the dispersion of the pyrite particles. Chloroform was subsequently added during the cooling process. After cooling, heavy precipitates ($\rho > \rho_{\text{solvent}}$) were removed by centrifugation, and ethanol was added into the reserved colloidal dispersion. After centrifugation, FSNC precipitates were collected and light ($\rho < \rho_{\text{solvent}}$) oxides remained with the upper solvent. The FSNCs were then washed with ethanol/chloroform mixed solvent to remove the non-chemical-adsorbed ODA. The solvent and ODA can be reused after distillation. Stable colloidal dispersion was obtained by dispersing the FSNC precipitate (2.5 g) in ODX/chloroform solution (1.6 mmol/L). The FSNCs can be reversibly precipitated again upon the addition of ethanol, and then dispersed in chloroform stably. FSNCs can be further purified by repeating the dispersion–precipitation process for two to three times. Finally, stable FSNC ink was prepared after dispersing in chloroform. Chloroform, ethanol, and excessive ODX can be reused after fractional distillation. For the drop-coating process, stainless steels (304 L) and glass substrates were cleaned in ethanol by ultrasonication before use. FSNC ink was drop-coated on the substrate, and then dried at room temperature. The structure and component of the film can be further regulated by heating in S vapor or N₂ gas.

The classical vulcanization process include placing clean stainless steel sheets in a sealed quartz tube, where O₂ was pre-excluded by N₂, heating at 450 °C for 4 h, and then cooling under the protection of N₂. For the testing devices, FSNC film was sandwiched between the stainless steel substrate (304 L, 0.03 mm thick) and the fluorine-doped tin-oxide (FTO) side of the conductive glass with a device structure of FTO/FSNCs/Fe. The light enters from the FTO glass into the FSNC film. The back of the stainless steel side was closely attached to a copper radiator to eliminate thermal effects.

3 Electrical test

Electrical tests were carried out on a CHI660D electrochemical workstation (Shanghai Chenhua, China). A voltage of 1.0 V was used for the resistivity tests. All the resistivity tests and IV tests were performed under dark condition.

Xenon lamp (1000 W/m²) equipped with a shadow shield was utilized as a light source for the photoconduction tests. The light (off-on) was controlled by the shadow shield. A voltage of 1.0 V was used for the photoconduction tests.

4 Characterization

Micro-morphology was observed via transmission electron microscope (TEM) (Japan electron optics laboratory co., ltd, Japan); ()VEGA II LMU scanning electron microscope (SEM) (Tescan, Czech) equipped with X-ray energy dispersive spectrometer (XEDS). Crystal structure was analyzed using D/Max-2500 X-ray diffractometer (XRD) (Rigaku, Japan). Fourier transform infrared spectroscopy (FTIR) was recorded on a Magna 550II FTIR spectrometer (Nicolet, the USA) via the KBr pellet method. Ultraviolet visible (UV-Vis) spectroscopy was recorded on a TU-1901 UV-Vis spectrophotometer (Beijing Persee, China). Particle size distribution was analyzed using the nano ZS90 zetasizer (Malvin, English).

Supplementary Figures

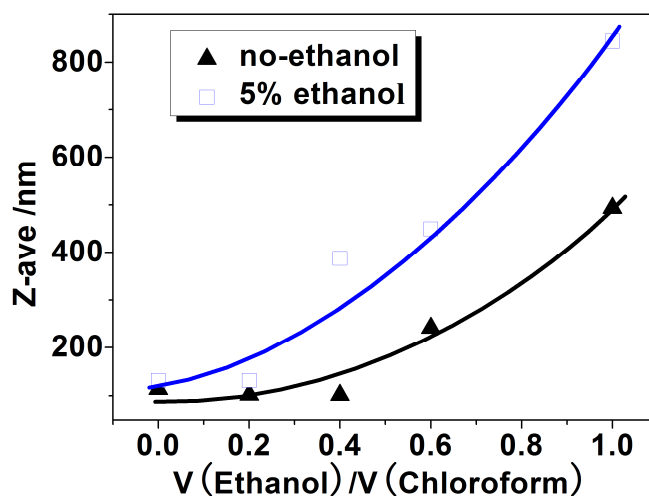


Fig.S1. Average size of FSNCs from different solvent: 1 re-dispersed in chloroform solvent; 2: re-dispersed in ethanol/chloroform mixed solvent(ethanol%=5).

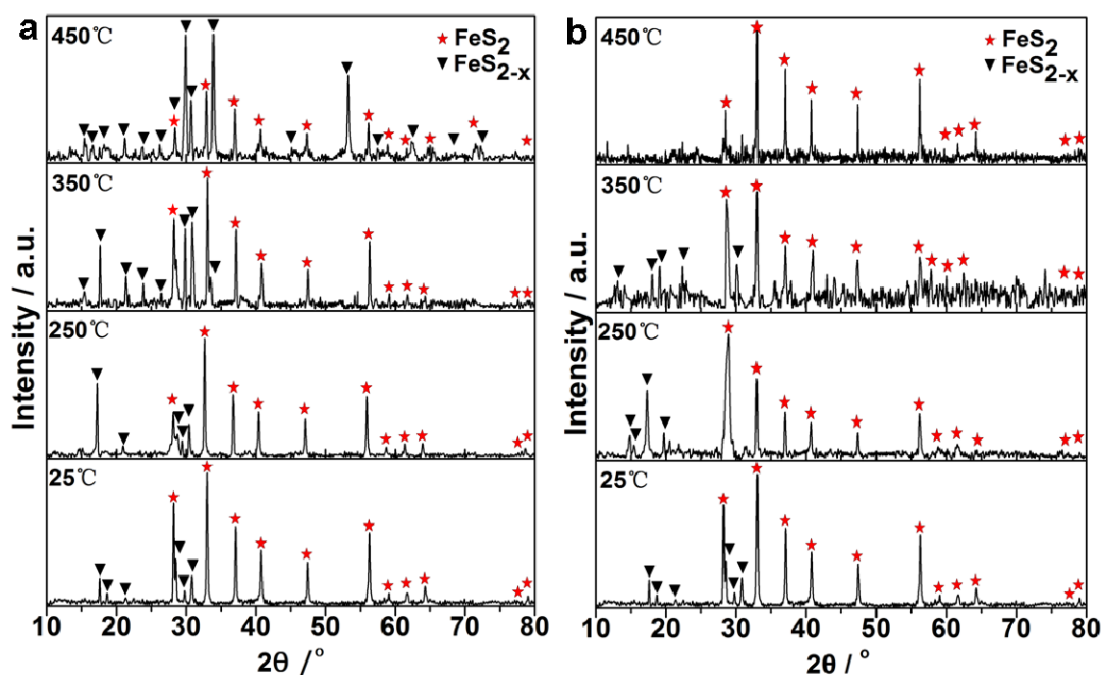


Fig.S2. XRD of FSNCs film sintered at different temperature: (a)in N_2 gas; (b)in S vapour.(FeS_2 : JCPDS 42-1340; Fe_7S_8 : JCPDS 29-0723; Fe_3S_4 : JCPDS 16-0713; FeS : JCPDS37-0477; Al_2SiO_5 :JCPDS 16-0602.)

Different FSNC films could be obtained after heated in S vapor at different temperature. After heated in S vapour at 450 °C for 4h, phases of low S/F ratio completely disappeared and transformed into FeS_2 phase. However, at a lower temperature, phase changes in the thin film become relatively complex. After heated at 250°C for 4h, some phases of the film disappeared, such as Fe_3S_4 , Fe_7S_8 and et al., but content of FeS phase was increased. After sintered at 350°C for 4h, FeS phase decreased, and other phases of low S/F ratio increased, such as Fe_3S_4 , Fe_7S_8 et al., The desulfurization reaction occurred.